

Arsenic form and distribution at the historic Alexander gold processing site, West Coast

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Abstract

The Alexander gold mine operated from 1924 to 1943, and was developed in orogenic veins of the Reefton goldfields on the West Coast. Preliminary studies have revealed high arsenic contents and other heavy metals at the Alexander Mine processing site. A roaster was used for a short period of time to liberate gold encapsulated in sulphide minerals, including arsenopyrite. Processing also included amalgamation, cyanidation and precipitation onto zinc plates. Residual processed material was dumped on site. Arsenic values of up to 38 wt% have been recorded by FP-XRF, as well as high zinc value of up 97,000 mg/kg and high Pb, Hg and Sb.

The government has announced a budget of \$3 million to clean up both the Prohibition (Waiuta) and Alexander Gold Mines on the West Coast (Victoria Forest Park). The Alexander site is on a flood plain, with the possibility of contaminated material being eroded away if the river changed its course or flooded. The scope of this study is to look at the metalloid distribution and mobilisation of arsenic as well as mercury, cyanide, lead, antimony and zinc at the site before remediation takes place. The area is administrated by the Department of Conservation and after clean-up it will be preserved as a historic site.

Keywords: arsenic, Alexander gold mine, Reefton goldfields, heavy metals, gold, environment, historic mine.

Introduction

The Alexander gold processing site is located on the true left bank of the Alexander River in the Victoria Forest Park on the West Coast (Fig. 1). The orogenic quartz reefs that were mined between 1921 and 1943 are located 740 m a.s.l. on the mountain above the processing site (Gage, 1948). Mineralisation occurs as free gold as well as encapsulated by iron sulphides, mostly arsenopyrite. Processing of this ore liberated and oxidised the arsenic as well as contributing heavy minerals through amalgamation, cyanidation and precipitation.

Hard rock mining in the Reefton goldfields dates back to 1870 with the Alexander mine the eight largest and the last historic mine to commence operating (Barry and Armstrong, 1993). No rehabilitation took place after closure of Reefton's historic mines, with many having elevated arsenic and heavy metal levels, such as Big River (Druzbecka and Craw, 2014), Prohibition (Waiuta) (Haffert and Craw, 2009), Bullendale (Haffert and Craw, 2010) and Golden Lead.

The government has announced a budget of \$3 million to clean up both the Prohibition (Waiuta) and Alexander mines (Smith, 2015). The Alexander processing site ranks second on the Government's Contaminated Sites Remediation Fund Priority List. Clean up at Alexander is scheduled to commence summer 2016.

The Alexander processing site consists of an Edwards Roaster (the roaster site) located 300 m northeast of the main battery and cyanidation plant (the battery site). This paper concentrates

on the arsenic contamination at the roaster site, with a brief mention of heavy metal and arsenic contamination of the battery site. Arsenic and heavy metal values were obtained using field portable x-ray fluorescence (FP-XRF).

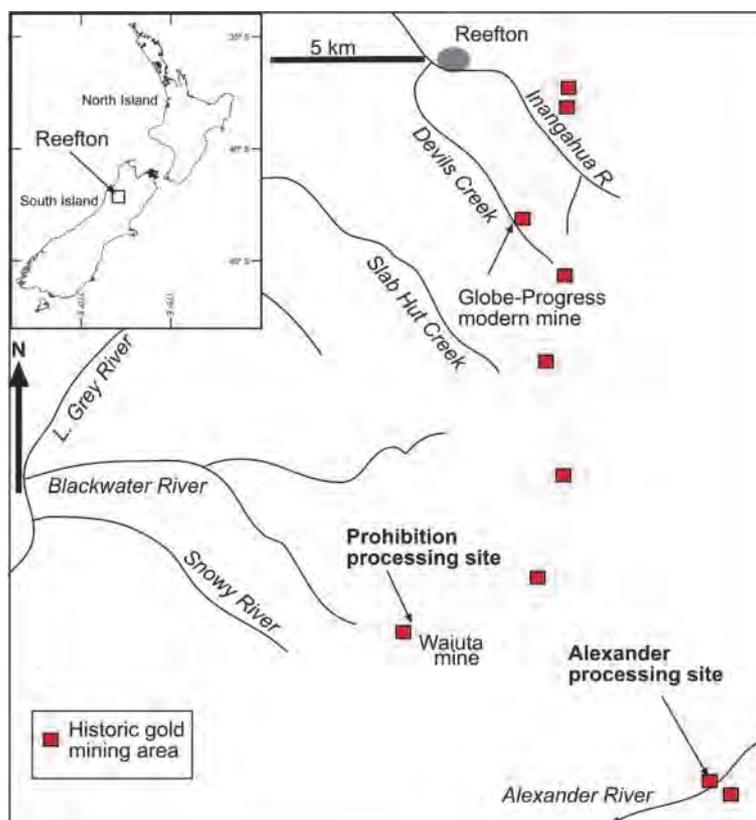


Figure 1. Location map of the Alexander mine and processing site.

Alexander roaster site

The roaster site has the intact brick remains of an Edward Roaster, wooden foundations of cyanide tank(s) and tailings from the roaster. Arsenic contamination on the site is largely confined to three red waste piles and inside the Edwards Roaster. The site is also contaminated with Zn, Pb, Hg and Sb.

Edwards Roaster

The Edwards Roaster is located approximately 15 m northeast of the red waste piles. It was built and commissioned in 1935 but was closed the following year due to losses during treatment thought to be caused by dusting inside the furnace (Webb 1936). The roaster was used to liberate gold encapsulated in sulphide minerals, mainly arsenopyrite. Arsenic trioxide gases were likely released straight into the atmosphere, and it was probably the precipitation of arsenolite inside the furnace that caused the dusting problem (Trumm, 2014). Cyanide boxes on the site were cleaned up and processed after the roaster was shut down.

High arsenic waste inside the remains of the roaster and on top of the flue comprises 47 m³ of material with an additional 6 m³ of roasted material in the flue. The highest values of arsenic on the roaster site are inside the flue, with FP-XRF values up to 38 wt% (sample dried and milled) but mostly around the 10-15 wt% mark. Crystalline growths on the flue roof and walls are comprised of a needle-like calcium arsenate mineral (Ca₃(AsO₄)₂) and gypsum

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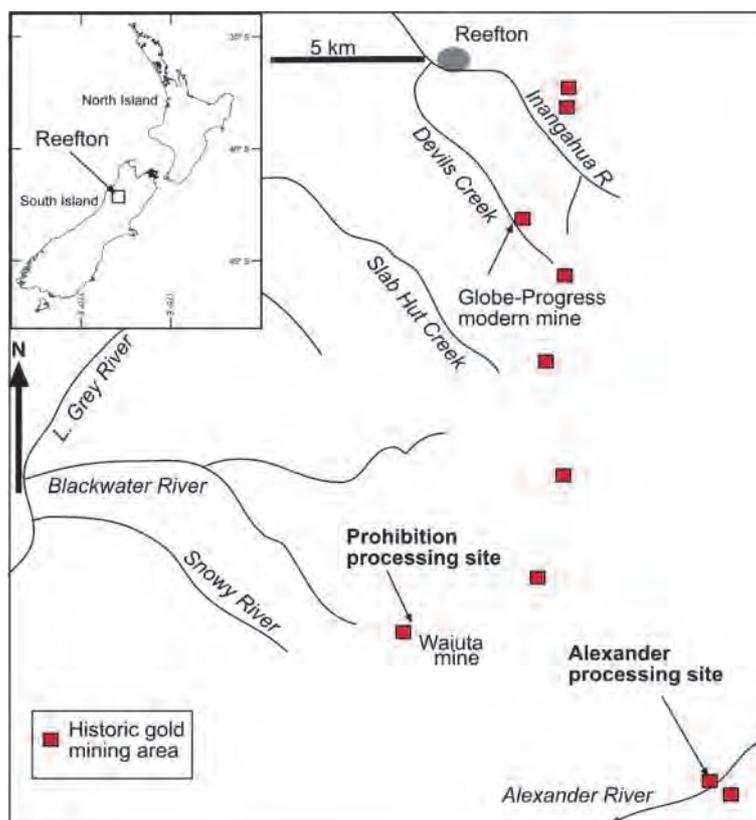


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($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), which may indicate the addition of lime during roasting (Bothe and Brown, 1999), as well as possible claudetite (As_2O_3) (Fig. 2). Mercury sulphide has been identified from dust on the chimney walls. Paste pH of the material within the roaster and the flue varies from 4.93 to 7.09. The brickwork on the outside of the roaster and the soil immediately surrounding the roaster are low in arsenic (mostly $< 200 \text{ mg/kg}$).

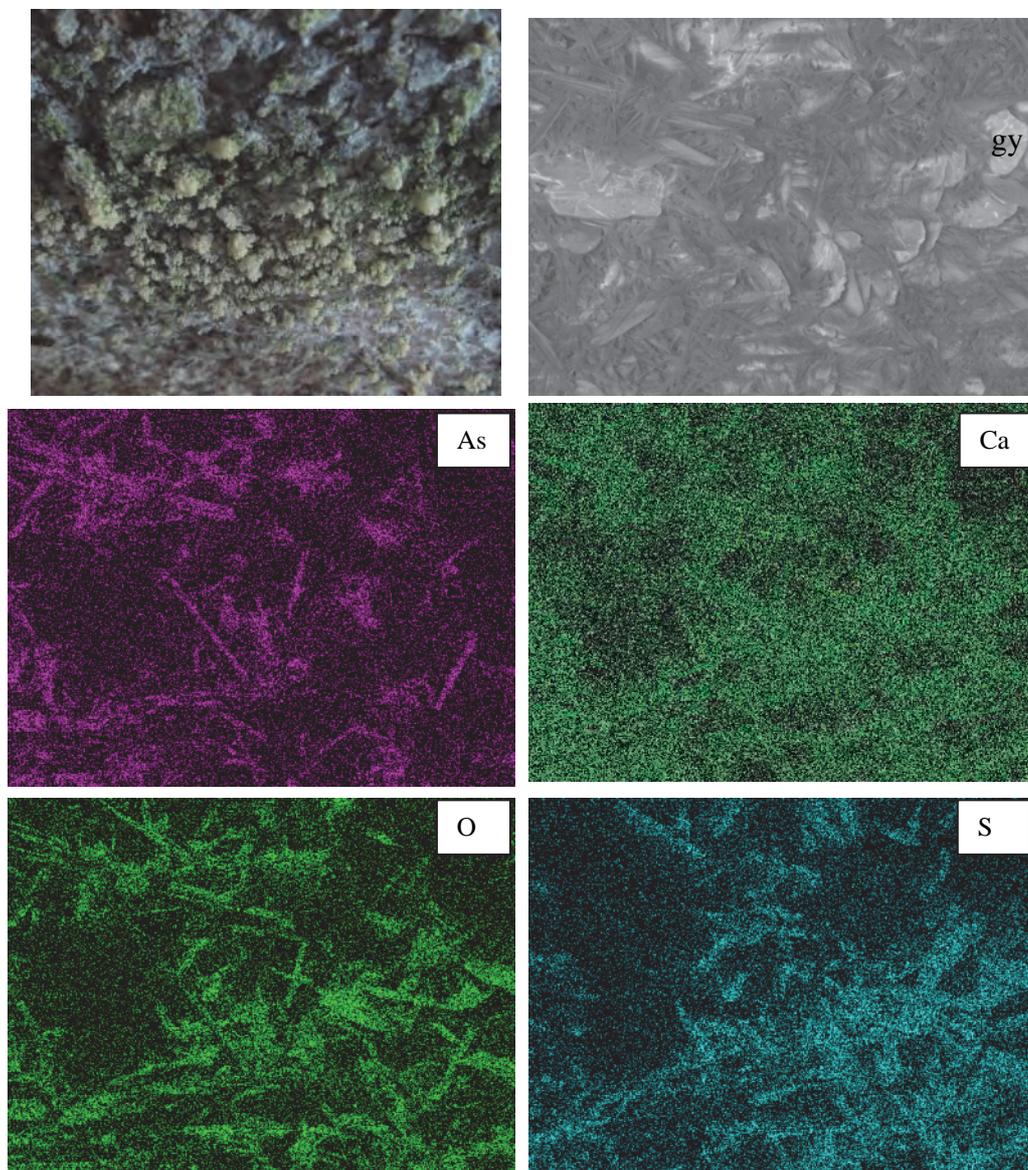


Figure 2. Crystalline growths on the roof of the Edwards Roaster flue. The SEM image shows the presence of a needle-like calcium arsenate mineral and plates of gypsum. Element maps of arsenic (As), calcium (Ca), oxygen (O) and sulphur (S).

Red waste piles

Residual processed material was dumped on the roaster site into three red waste piles comprising approximately 600m^3 (Fig. 3). A 4WD track crosses over, flattens and attenuates the west edge of the westernmost pile. The southernmost pile is immediately adjacent to and above a small creek that cuts through the alluvial terrace. The elongated eastern pile runs sub-parallel to the creek.



Figure 3. Red waste piles at the roaster site. a) red pile that is crossed by the 4WD drive track on the left, b) the long red pile that runs parallel to the creek with exposed waste on top.

The piles are completely oxidised and consist of mostly quartz and iron oxide with minor clay aluminosilicates and scorodite, a hydrated iron arsenate mineral ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) (Fig. 4). There is also a calcium arsenate mineral present but the grain size is small ($< 20\mu\text{m}$). FP-XRF values of arsenic up to 35,000 mg/kg (sample dried and milled) have been recorded in the red piles. Paste pH of the red piles varies from 5.27 to 6.41. Scorodite stability, and therefore arsenic mobility, is controlled by the acidic and oxidised nature of the red waste piles. Arsenic solubility from scorodite is high in strongly acidic or alkaline pH soils (Krause and Ettel, 1989, Fujita et al., 2011). The red piles are homogenous with depth, with a sharp transition to clayey silts then alluvial sands over 10-15 cm immediately above the river terrace boulders. Arsenic is elevated in the alluvials ($< 2,000$ mg/kg), although some of this arsenic will be from contamination during augering.

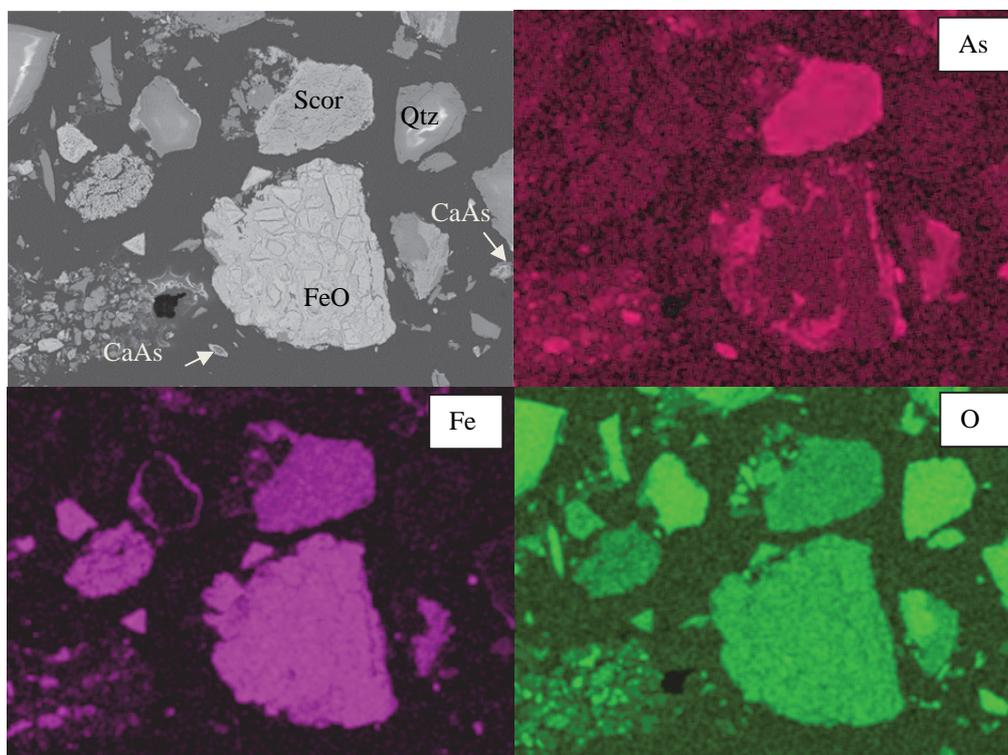


Figure 4. SEM image of the red waste pile material (AMR10), with scorodite (Scor), quartz (Qtz), iron oxides (FeO) and a calcium arsenate mineral (CaAs) and element maps for arsenic (As), iron (Fe) and oxygen (O).

Arsenic contamination of the site, excluding the Edwards Roaster, is very easily identified visually by the colour of the soil. Contaminated waste is a bright brick red colour, while the alluvial sands are a light yellowish brown colour. A lateral profile across the edge of one of the red piles and into the soils of the alluvial sands shows a gradual reduction of the red colour, with associated reduction of arsenic contamination as well as Fe, Pb and Zn values (Fig. 5). The correlation of soil colour to arsenic contamination could be used as a guide to allow for a quick clean-up of the site which can be later checked with FP-XRF when the remediation is complete.

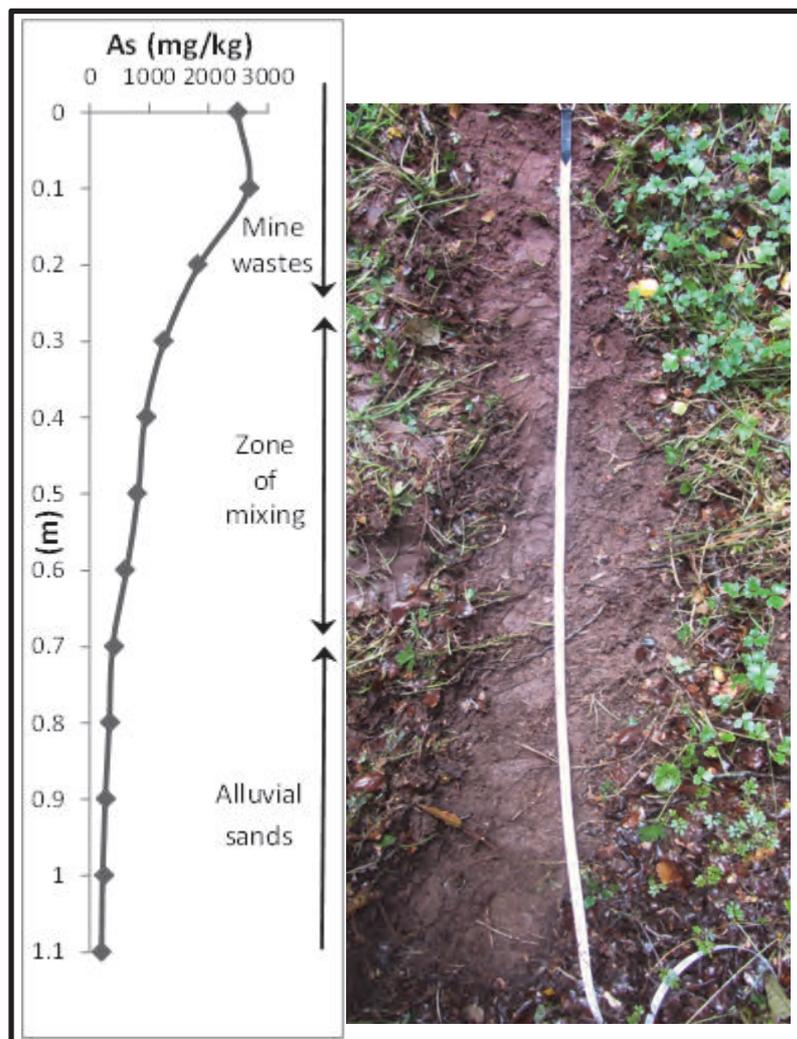


Figure 5. Lateral section from the side of one of the red waste piles into the alluvial sand soils.

Field portable x-ray fluorescence grid

A FP-XRF grid was completed using an Innov-X machine in soil mode with a 30 second count time. A 3 m grid spacing was done over the roaster site, with a 1 m grid over and around the Edwards Roaster, including spot checks of the inside and outside of the brickwork (Fig. 6). The grid was completed to define the extent of the arsenic contamination as well as to identify heavy metal contamination.

The Edwards Roaster flue has the highest arsenic values on the site. The flue and roaster have extremely high As (up to 530,000 mg/kg) and elevated Hg (up to 1,400 mg/kg), Sb (600 mg/kg), W (up to 600 mg/kg), Zn (up to 1,800 mg/kg) and Pb (up to 900 mg/kg). The Fe

(up to 180,000 mg/kg) and Ti (up to 1,600 mg/kg) contents are a lot lower than that of the red piles. For the 3 m site grid, arsenic contamination was highest in the red piles with values of up to 13,000 mg/kg. The red piles had the highest Fe (up to 385,000 mg/kg), Ti (up to 6,900 mg/kg) as well as elevated Pb (up to 350 mg/kg) and Zn (2,300 mg/kg). There is a trace of Hg, Sb and W associated with the higher arsenic values in the red piles.

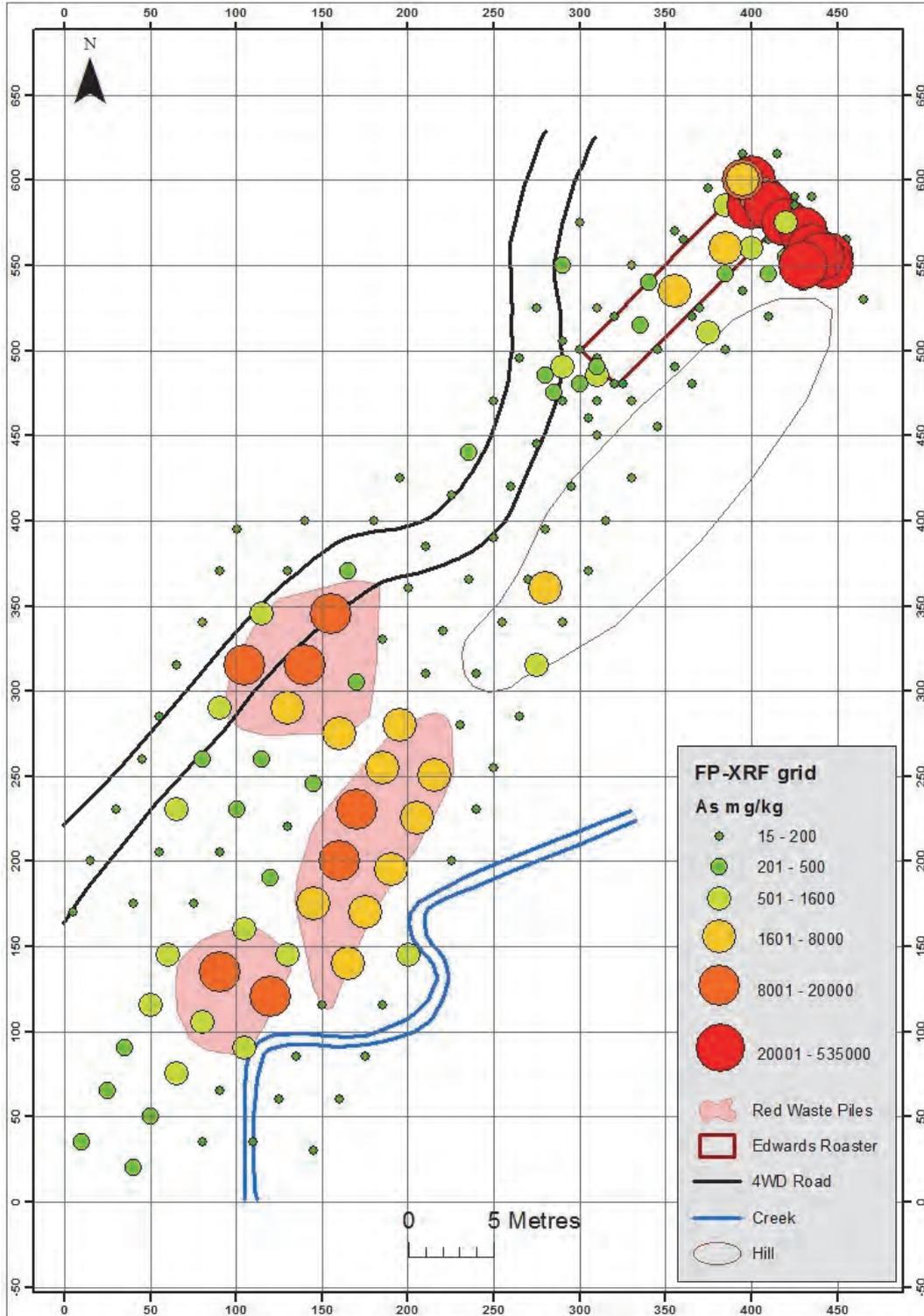


Figure 6. FP-XRF grid over the roaster site, showing arsenic values, with high values in the three red waste piles and flue of the Edwards Roaster.

Moisture content and sample homogeneity can affect the results from the FP-XRF. A FP-XRF will give relatively good results for samples with 5-20 % moisture content, anything with a moisture content over 20% will be under-estimated (Laiho and Perämäki, 2005). The roaster site is covered in secondary Beech (*Nothofagus sp.*) growth forest, protecting the site from evaporation (Fig. 3). There is often permanent standing water in depressions in the 4WD road, including where the road crosses over one of the red piles. Representative samples were taken of the red piles at surface and at depth, in contaminated alluvials, road samples and material within the Edwards Roaster, over a range of arsenic values and moisture contents. Moisture contents ranged from 10-42 %, with over half of the samples having moisture contents greater than 20 %. Preliminary results show that there is a greater variation in arsenic values between wet and dried sample than between dried and milled samples, especially for saturated samples with greater than 20,000 mg/kg As (Fig. 7). Samples will be sent off to the laboratory for XRF, in order to calibrate the FP-XRF grid.

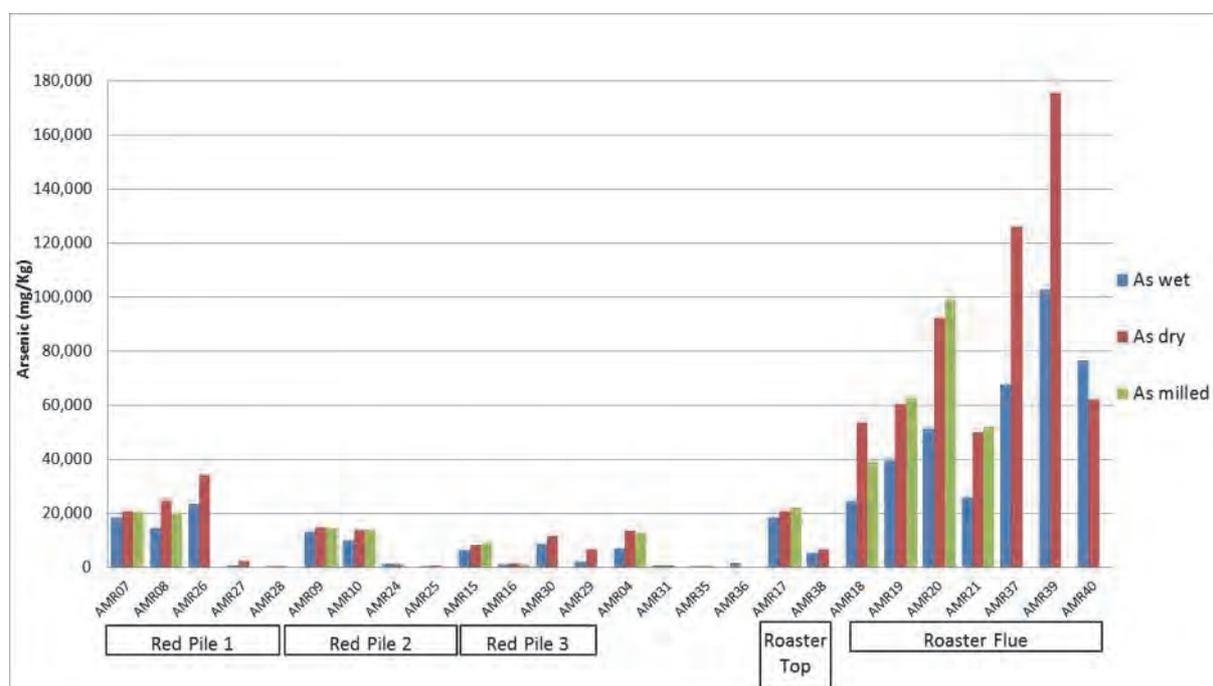


Figure 7. Arsenic values of roaster site samples showing the difference in FP-XRF arsenic values between wet, dried, and dried and milled samples. Note that some samples are in the process of being milled.

Re-vegetation and remobilisation of arsenic and heavy metals

The red waste piles have moderate slopes and are covered in grasses and creeping buttercup (*Ranunculus repens*) with minor fern species (Fig. 3). Soils are thin to non-existent with exposed red waste material at the top of the piles. FP-XRF of sapling beech tree leaves and stems (*Nothofagus sp.*) that were growing on the waste pile closest to the creek, indicate elevated levels of As, Fe, Zn, Cu compared to a control sample growing 150 m south of the site. Beech trees also grow in contaminated waste material (up to 100,000 mg/kg As) at the battery site. FP-XRF has been proven to be a useful indicator of contamination in fresh plant material, however, like in-situ soil measurements, the moisture content in the plants will affect the results (Gutiérrez-Ginés et al., 2013). Elevated As, Fe and Zn values are also seen in buttercup and fern samples taken from the red waste piles, but to a lesser extent.

The outside brickwork of the Edwards Roaster was covered in a thick layer of moss which has since been sprayed by DOC in preparation for site clean-up. The inside of the roaster, which is exposed to the environment, is sparsely covered in ferns, mosses, grasses and sapling trees including Horopito (*Pseudowintera colorata*) (Fig. 8). FP-XRF of sapling Horopito leaves and stems show elevated As, Fe and Zn. Native hook grass (*Uncinia uncinata*) grows on top of the flue in arsenic contaminated soils (up to 9,500 mg/kg) with high Zn (up to 1,800 mg/kg). There is no vegetation growing on the inside of the flue.



Figure 8. Alexander roaster site. a) Looking south from the top of the Edwards Roaster, with sparse vegetation growing inside the roaster, mainly ferns and mosses with Horopito (*Pseudowintera colorata*) saplings. b) Secondary regrowth forest, predominantly Beech (*Nothofagus sp.*), with 4WD track and roaster on the left c) Hook grass (*Uncinia uncinata*) growing on top of the flue.

Alexander battery site

The battery site consists of the foundations and remains that use to house an ore pass, 10 stamp battery and Wilfley table with 15 cyanide tanks, 3 zinc boxes and tailings. The battery is built on up on a terrace with a small creek/wetlands below that drains the site. Floods have helped deteriorate the site, and have likely removed some of the tailings. The battery site is characterised by very high levels of Zn (up to 97,000 mg/kg) and Pb (up to 4,000 mg/kg) in the vicinity of the cyanidation plant and small areas of elevated As (up to 100,000 mg/kg) in the two boxes of cemented material. Abundant arsenopyrite and pyrite as well as some scorodite are present in the cemented material as well as quartz and aluminosilicates and minor barite and a zinc copper oxide mineral.

Conclusion

The Alexander site is contaminated with arsenic and other heavy metals from more than 20 years of gold processing. Arsenic contamination at the roaster site is largely confined to inside the Edwards Roaster and the three red waste piles. Arsenic values up to 38 wt% have been recorded inside the roaster. The red waste piles have arsenic values up to 35,000 mg/kg mainly in the form of scorodite with minor tiny grains of a calcium arsenate mineral. It is likely that in the 80 years that the waste piles have been sitting exposed that most of the highly soluble calcium arsenate and arsenolite has weathered to scorodite. A moderately acidic soil paste pH and the oxidised nature of the red piles means that the scorodite, and therefore arsenic, should be stable as long as environmental conditions do not change. The sparse nature of the vegetation growing on the red waste piles could be due to a variety of factors, not just arsenic and heavy metal contamination. The lack of soil development, moderate slope of the piles and sandy nature of the soil resisting water retention, as well as poor substrate chemistry (mostly iron oxide and quartz) could all contribute to the lack of development of native forest.

There is abundant arsenopyrite and pyrite in the cemented material at the battery site, indicating that the material underwent different processing to the red waste piles at the roaster site. The sulphides appear to be semi-stable with only minor development of scorodite. The cemented material in the boxes was likely partially processed ore that was to be shipped to Australia for further processing, after the roaster was decommissioned. The battery site also differs to the roaster site, in having very high zinc values.

FP-XRF proved to be a quick and reliable field method for showing relative contamination but should not solely be relied upon for exact values. Unique to the Alexander site, the colour of the soil can be used as a guide to allow a quick clean-up of the roaster site. FP-XRF can also be used to give an indication of contamination uptake by plants.

Acknowledgements

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